

Studies of Localized Corrosion in Welded Aluminum Alloys by the Scanning Reference Electrode Technique

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TECHNICAL PAPER

STUDIES OF LOCALIZED CORROSION IN WELDED ALUMINUM ALLOYS BY THE SCANNING REFERENCE ELECTRODE TECHNIQUE

INTRODUCTION

Overall corrosion rates of welded aluminum alloys are generally higher than the parent metal, based on previous electrochemical studies ¹ ² made with 2219-T87 Al-Cu and 2195 Al-Li alloys, both welded autogenously and with 2319 (Al-6Cu) filler wire. The 2195 alloy showed localized corrosion as well. The corrosion rate increase in autogenously welded 2090 Al-Li alloy was somewhat less pronounced compared to the other two. Stress corrosion results for the 2195 alloy ³ ⁴ have indicated an increased susceptibility to stress corrosion for welded samples (2319 filler), also consistent with an increase in the overall corrosion rates for the welded samples. A recently developed technique called the scanning reference electrode technique (SRET) allows the measurement of localized corrosion. This new technique is used in this study in an attempt to understand the general corrosion on a microscale. The Al-Li alloys 2195 and 2090 welded with 4043 (Al-5.2Si) and 2319 filler materials were used for the study. The results are compared with commonly used Al-Cu 2219 alloy welded with the 2319 filler.

THE SCANNING REFERENCE ELECTRODE TECHNIQUE

The SRET instrument shown in figure 1 is commercially available from EG&G Princeton Applied Research Corporation (EG&G-PARC). It has the capability to measure micro galvanic potentials close to the surface of materials, and it allows in situ examination and quantification, on a microscopic scale, of electrochemical activity as it occurs. The SRET is microprocessor controlled, and electrical potentials are measured by a special probe capable of translation in the X- and Y-directions. The specimen in the form of a cylinder is held in a vertical position and rotated around the Y-axis. The scan is synchronized with a display monitor and the resultant data are shown in the form of line scans of two-dimensional area maps. The width of the area maps (X-direction) can be set at will using the zoom-in feature of the experimental setup. The height of the area maps (Y-direction) is set automatically by the control software according to the proper aspect ratio. Movement of the scanning probe during data collection is in the Y-direction. Direct measurement of surface potentials, showing anodic and cathodic areas, at discrete positions on the sample surface, may be taken and stored for time-related studies. Because the minimum detectable signal (MDS) is of the order of 1 mA/cm², a potential must be applied to the sample to increase the corrosion current to at least this level, accomplished by means of a separate potentiostat (EG&G-PARC model 273A Potentiostat/Galvanostat) coupled to the SRET system.

EXPERIMENTAL PROCEDURE

Corrosion specimens consisted of cylindrical metals rods 10.2-cm (4-in) long. Rod diameters were approximately 1.2 cm (0.48 in), but varied slightly from sample to sample. In the case of the welded samples, longitudinal V-grooves 0.318-cm (0.125-in) deep were machined along the entire length of the rods. The V-grooves were then filled using either 4043 or 2319 filler by tungsten inert gas (TIG) welding and subsequently machined down to a smooth circular surface approximately 1.14 cm (0.45 in) in diameter.

For each experiment, the test specimen was mounted in the collet of the SRET system, and the probe, counter electrode, and reference electrode were placed in their proper positions in the machine. The probe was then driven to a position such that the point was approximately 0.5 mm from the metal cylinder, and the entire assembly was immersed in a corrosive medium consisting of 3.5-percent sodium chloride solution. About a 5.1-cm (2-in) length of the metal sample rod was thus exposed to the corrosive medium. A potential approximately 150-mV noble to the normal corrosion potential (E_{corr}) was applied to each metal rod by the potentiostat. During data collection, the sample was rotated at 100 revolutions per minute (r/min). Map scans were taken beginning and ending at equal distances from the zero point of the SRET system, such that a distance of 3.0 cm of the sample circumference was displayed on each map (X-direction). In the case of welded samples, the weld was positioned as nearly as possible to a position 180° from the zero point of the SRET system so that the welded area appeared close to the middle of the map scan. The experiments were set up in such a way that all maps had a width of 3.0 cm (X-direction) and a height of 2.25 cm (Y-direction). Movement of the probe during the scan was in the Y-direction. Each scan was recorded after a delay of 2.5 h with the sample at the appropriate potential. The current after this period varied from 2.3 to 2.5 mA/cm² for all samples. After data collection was completed, each map was displayed on the computer screen and the proper palotte for display of the map features (potentials for anodic and cathodic features) was obtained using software developed by EG&G-PARC for this purpose, cathodic features being positive and anodic features being negative.

RESULTS AND DISCUSSION

Localized Corrosion in the 2219-T87 Alloy

An area map scan for the wrought 2219-T87 alloy is shown in figure 2. The scales of all maps are expanded by a factor of approximately 4 over those actually occurring in the samples. As seen from the map of figure 2, anodic and cathodic features are interspersed, and there are not a great many distinct features.

A map scan for the 2219 alloy welded with 2319 filler is shown in figure 3. The map features are highly striated parallel to the weld direction (Y-direction). The area containing the weld bead is strongly cathodic, with strong anodic strips bordering the cathodic region. These anodic regions are, therefore, subject to severe corrosion. The width of the melted region was about 0.90 cm on the sample rod, while the width of the cathodic region on the map is about 1.1 cm on the map scan. The cathodic region thus extends slightly into the heat-affected zone (HAZ).

Localized Corrosion in the 2090 Al-Li Alloy

An area map scan for wrought 2090 Al-Li is shown in figure 4. The map shows that anodic and cathodic features are generally not interspersed, but exist in rather broad zones that are either anodic or cathodic. Within each zone, there are several features of the same sign that are stronger and more numerous than were those for the wrought 2219-T87 alloy.

A map scan for the 2090 alloy welded with 4043 filler is shown in figure 5. Here, the features are striated in the Y-direction, with the weld bead being strongly cathodic. Strong anodic regions border the cathodic region containing the weld bead, which was measured as 1.0 cm on the map. The width of the melted region was about 0.7 cm on the sample rod. Thus, the cathodic region extends slightly into the HAZ, as in the case of the 2219-T87 alloy.

A map scan for the 2090 alloy welded with 2319 filler is shown in figure 6. Here the features are again highly striated. The region containing the weld is strongly cathodic, with strong anodic regions adjacent to the weld. The width of the cathodic region is 0.93 cm on the map, while the width of the

melted weld bead was measured as 0.6 cm on the sample rod. Again, the cathodic region extends slightly into the HAZ. The regions bordering the weld are again subject to severe corrosion.

Localized Corrosion in the 2195 Al-Li Alloy

A map scan for the wrought 2195 alloy is shown in figure 7. Here, the anodic and cathodic regions are rather broad, occurring in an alternating sequence in the X-direction. Many strongly anodic or cathodic features of the same sign comprise each region. The pattern is similar to that observed for the 2090 wrought alloy.

A map scan for the 2195 alloy welded with 4043 filler is shown in figure 8. The pattern is highly striated in the direction of the weld (Y-direction). The width of the weld bead, as measured on the sample surface, was 0.75 cm, while the width of the cathodic region on the map is 0.95 cm. Thus, the cathodic region again extends slightly into the HAZ. Very strong anodic regions border the cathodic region containing the weld bead, so that these regions are highly subject to corrosion.

The map scan for the 2195 alloy welded with 2319 filler is shown in figure 9. This map strongly resembles that for the sample welded with 4043 filler, in that the cathodic region containing the weld bead is very strong, as well as are the anodic regions at its borders. The width of the cathodic region is 1.0 cm on the map, while the width of the melted region was measured as about 0.7 cm on the sample rod. As in all previous cases, the cathodic region extends slightly into the HAZ. As with the other highly striated welded samples, the regions bordering the cathodic regions are subject to severe corrosion.

Correlation With Previous Corrosion Rate Measurements

As mentioned previously, electrochemical corrosion studies using the dc polarization resistance technique have indicated that welding increases the corrosion rates for the 2219-T87 alloy and the 2195 Al-Li alloy, both for heterogeneously welded (2319) filler and autogenously welded samples. These observations are also supported for the 2195 Al-Li alloy by stress corrosion studies, where it was found that welded samples (2319 filler) were more subject to stress corrosion than the wrought material. Studies of the 2090 Al-Li alloy have not been conducted by this method. Studies of heterogeneously welded 2090 alloy have not been carried out using the polarization resistance method, but a study of the autogenously welded material using this method indicated that the corrosion rate is less affected by autogenous welding.

The present studies of localized corrosion in welded samples show that the cathode areas are considerably increased for all alloys. The areas containing the welds are strongly cathodic for all samples studied. These results suggest a reduced anode/cathode ratio, and hence an overall increase in corrosion rate, thus explaining the previous corrosion results obtained by using the polarization resistance technique for the overall corrosion rates for flat samples. Although electrochemical studies of corrosion rates for the heterogeneously welded 2090 have not been carried out yet, studies of the autogenously welded 2090 material using the electrochemical method indicate that the corrosion rates were not as greatly increased by autogenous welding. However, an increased anode/cathode ratio may be responsible for the observed smaller increase in corrosion rate.

It is interesting to note that the weld bead and a part of the HAZ is cathodic in all cases, irrespective of the filler wire chemistry while the parent metal is anodic. This result may be attributed to the differences in the microstructure of the alloy in the fusion zone and the HAZ. These areas contain as-cast and overaged structure, respectively. The parent metal is artificially aged to peak hardness and is anodic to the weld. A detailed explanation of this behavior is contained in the appendix.

SUMMARY

Studies of localized corrosion in welded 2219-T87 Al (2319 filler), 2090 Al-Li (4043 and 2319 fillers), and 2195 Al-Li (4043 and 2319 fillers) were carried out using the scanning reference electrode technique (SRET). Anode/cathode ratios were significantly smaller for the test specimens and apparently led to higher overall corrosion rates for these materials. These results are consistent with the results from previous studies of overall corrosion rates in the same materials obtained by the polarization resistance method. Also, in all samples, the weld beads were cathodic and the cathodic areas extended slightly into the HAZ. All of the weld areas were bordered by strong anodic regions, indicating a high propensity for corrosion in these areas. The cathodic nature of the weld may be attributed to its overaged microstructure.

REFERENCES

- 1. Walsh, D.W.: NASA/ASEE Summer Faculty Fellow, August 1995.
- 2. Danford, M.D.: "A Corrosion Study of 2090 Al-Li Alloy." Memorandum EH23 (94–76), September 6, 1994.
- 3. Torres, P.D.: "Stress Corrosion Evaluation of Aluminum-Lithium Alloy 2195 Welds and Weld Repairs." Memorandum EH24 (95–07), March 14, 1995.
- 4. Torres, P.D.: Unpublished results.



Figure 1. The scanning reference electrode system.

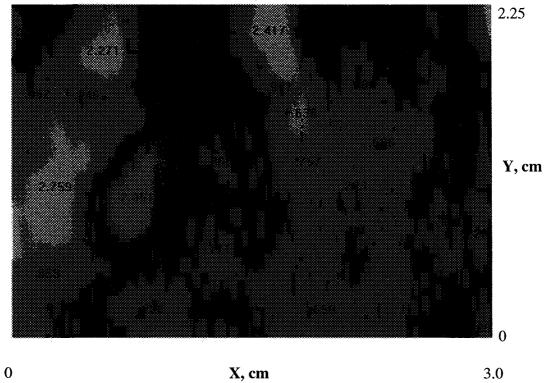
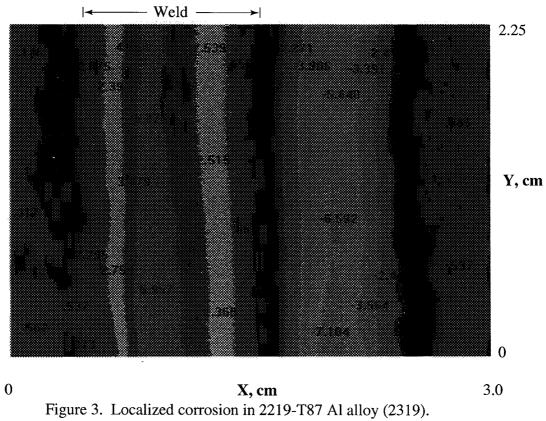
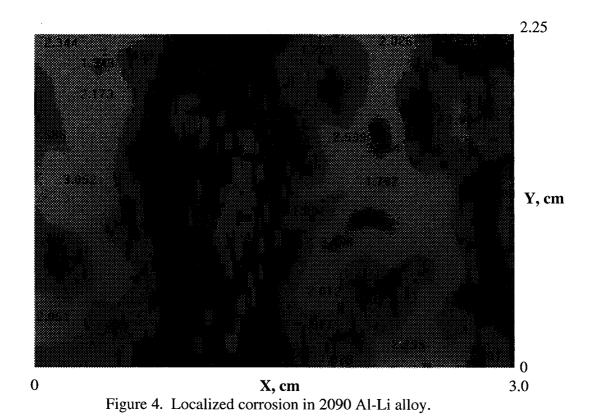


Figure 2. Localized corrosion in 2219-T87 Al alloy.





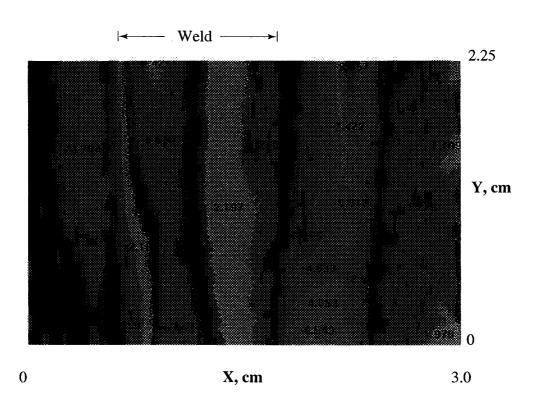
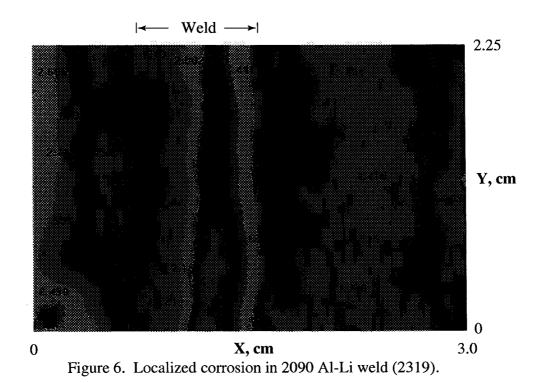
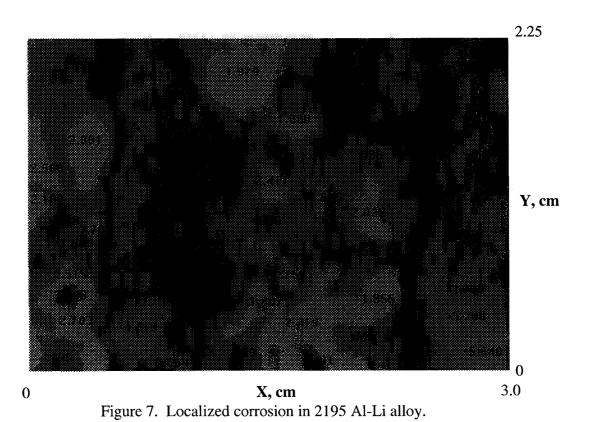


Figure 5. Localized corrosion in 2090 Al-Li weld (4043).





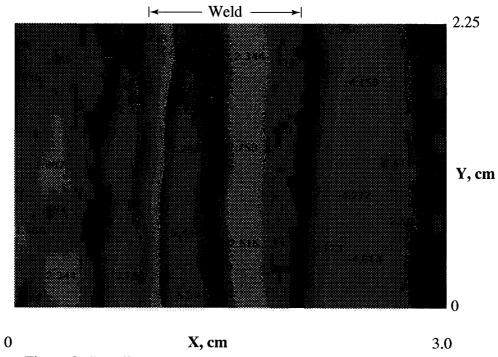
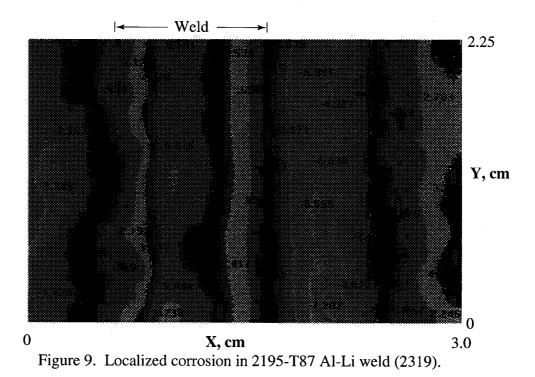


Figure 8. Localized corrosion in 2195-T87 Al-Li weld (4043).



APPENDIX

Explanation of Corrosion Effects in Aluminum Alloy Welds

Copper has a strong effect upon the tendency of aluminum alloys to corrode. Whatever produces a gradient in copper composition in the α -aluminum phase produces microscopic galvanic potential differences that accelerate corrosion and promote a macroscopic anodic tendency. Thus, overaged aluminum-copper alloys are cathodic with respect to underaged alloys, in which the copper gradients are more pronounced adjacent to the precipitate (Cu-Al₂) θ -phase, particularly at grain boundaries where θ -phase predominates.

The θ -phase itself has a solution potential equivalent to the anodic potential of α -aluminum with approximately 2.5-percent Cu dissolved. Hence, this phase can be anodic (>2.5-percent Cu in α) or cathodic (<2.5-percent Cu in α) depending upon the α -aluminum phase composition.

The general patterns of corrosion tendency around the welds are consistent with:

- Leveling of solute concentration in the α -phase in the weld fusion zone (FZ) due to relatively long high-temperature exposures
- Partial redessolving of solute near the θ -phase in the unmelted α -phase in the HAZ close to the FZ at lower temperatures and shorter exposures
- Unaffected parent metal at the conclusion of the HAZ.

Thus, there should be a highly cathodic region centering on the weld FZ, an anodic region in the HAZ just outside the FZ created by the residual solute gradients from the brief redissolving process, and eventually the corrosion tendency should rise back up to the level of the parent metal.

Lithium, unlike copper, is more active than aluminum and, where copper promotes a (local) cathodic tendency, lithium promotes an anodic tendency. Tying the Li up in the Al-Li) δ -phase is said to reduce the pitting tendency. Since aluminum is also reactive and depends for its corrosion resistance upon the formation of a protective surface layer, the major effect of Li should lie in its difference from aluminum and its tendency to disturb the protective film. One would not expect Li with its greater similarity to aluminum to have the large effect on corrosion that Cu does. Since even in the 2090 alloy there is sufficient Cu to yield a substantial corrosion effect, it is supposed that the very similar cathodic-anodic patterns about all welds are essentially a Cu effect.

Dissolved silicon has little effect upon the cathodic-anodic potential of α -aluminum. The silicon phase, although it is cathodic with respect to the α -aluminum, polarizes so as to limit the corrosion current from this source. Hence, not much corrosion effect should be expected when weld wire is switched from 2319 to 4043 aluminum.

Reference

Hollingsworth, E.H., and Hunsicker, H.Y.: "Corrosion of Aluminum and Aluminum Alloys." ASM Metals Handbook, Ninth Edition, vol. 13, Corrosion, pp. 583–609.

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